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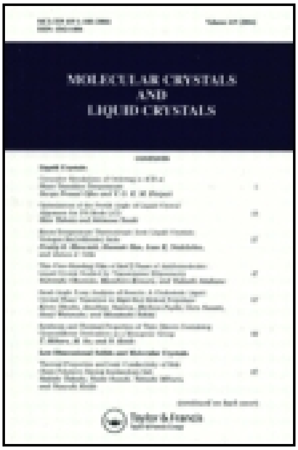

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Electro-Optical Properties of Low Molecular Weight Liquid Crystal/Copolymer Mixtures

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Electro-Optical Properties of Low Molecular Weight Liquid Crystal/Copolymer Mixtures

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Polymer dispersed liquid crystal (PDLC) films can be switched electrically from a light scattering off-state to a highly transparent on-state. Mixtures including different amounts of a high molecular weight copolymer and the eutectic nematic low molecular weight liquid crystal E7 were prepared in acetone which acts as a common organic solvent. PDLC films were obtained by a solvent induced phase separation (SIPS) initiated by evaporation of the solvent. The optical transmission properties of the obtained PDLC films were investigated as a function of composition, film thickness, and amplitude of the applied AC voltage. The electro-optical curves depend on the liquid crystal content and are highly reproducible. The particular properties of the copolymer allow to obtain a strong physical polymer network which in turn leads to well defined films compared to results obtained for other linear polymer/E7 systems.

Keywords: Polymer Dispersed Liquid Crystal; copolymer; nematic liquid crystals; electro-optical properties; phase separation

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INTRODUCTION

In recent years, dispersions of micron-sized liquid crystal (LC) domains in a polymer matrix (Polymer Dispersed Liquid Crystals - PDLCs) have found considerable potential for a variety of optoelectronic applications[1,2]. In the so-called normal mode, PDLC films can be electrically switched from a light scattering off-state to a transparent on-state. The electro-optical properties of polymer/LC blends strongly depend on the size, shape, number density and spatial distribution of LC domains.

One of the earlier techniques of PDLC processing is the solvent induced phase separation mechanism. The polymer and the low molecular weight LC (LMWLC) are mixed together in a common organic solvent. During evaporation of the solvent, phase separation occurs between the polymer and the LMWLC[3,4]. Films prepared by this method are sometimes not well characterized and exhibit generally less reproducible electro-optical properties.

An eutectic nematic mixture of cyanoparaphenylene derivatives (E7, Merck) was used as LMWLC material. The copolymer polyvinyl-difluoro-ethylene-hexafluoropropylene (PVDF-HFP) chosen in this work shows a strongly reduced miscibility with the LMWLC partially due to the presence of fluorine atoms. Furthermore, PVDF-HFP presents both amorphous and crystalline regions at room temperature even in the presence of LMWLC.

The optical transmission properties of the obtained PVDF-HFP/E7 films have been investigated as a function of film thickness, composition, and amplitude of the applied AC voltage. The results are discussed in terms of the transmission values in the initial field-off state and after application of several voltage cycles. Threshold and saturation voltages are also analyzed.

EXPERIMENTAL PART

Materials

The nematic LMWLC used in this work was the commercial mixture E7 (Merck) containing essentially cyanoparaphenylene derivatives. It exhibits a positive dielectric anisotropy at T=20°C and a nematic-isotropic transition temperature T_{NI} = 61°C[5]. The copolymer PVDF-HFP was obtained from Atofina (France) and is characterized by a molecular weight of M_w=450000g/mol and a polydispersity M_w/M_n=2.6.

Sample preparation

x weight-percent (wt%) of E7 (x=40, 50, 60, 70) and (100 - x) wt% of the copolymer were dissolved in a common organic solvent (acetone) at room temperature. The resulting mixtures were stirred mechanically until the blends became homogeneous. A small quantity of a blend was cast on a 100 μm thick polyethyleneterephthalate (PET) sheet (Renker, Germany), coated with a thin transparent layer of conducting indium-tin-oxide. The thickness and the uniform application of the mixtures were controlled by using a bar-coater (Braive, Belgium). The sample was dried at room temperature and after complete evaporation of acetone, another PET sheet was put on top of the first one.

For each composition, a large number of samples were prepared to check for reproducibility and to cover a range of film thicknesses varying from 5μm to 30μm. The film thickness was measured by a micrometer calliper (Mitutoyo; uncertainty: ±1 μm).

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Electro-optical measurements

The electro-optical experiments were performed at room temperature by measuring the transmission of unpolarized HeNe laser light at a wavelength of λ =632.8 nm. The PDLC films were oriented normal to the laser beam. The transmission measurements were corrected using appropriate calibration standards.

For electro-optical measurements, an external electric field was applied across the PDLC film. Starting from the electrical off-state, the applied sinusoidal voltage of frequency 145 Hz was increased continuously up to a desired maximum value V_{max}. Subsequently it was decreased in the same way. The whole scan up and down ramp was performed during 120 s and an additional measuring time of 60 s allowed to follow the relaxation behavior of the transmittance in the off-state. The same procedure was repeated several times using the same sequence of appropriate voltage maximum values.

RESULTS AND DISCUSSIONS

Figure 1 shows the transmission in the initial off-state (T_{OFF}) as a function of film thickness in a logarithmic representation. The LMWLC range from 40wt% to 70wt% has been covered in this figure. In general the optical transmission of PDLC films can be described by the Lambert-Beer law used in light absorbing systems[6] :

$$-\log T = -\log (I_T/I_0) = N_v \, \sigma \, d \qquad (1)$$

where T represents the optical transmission, I_T is the transmitted intensity, I_0 is the incident intensity, N_v is the number density of LMWLC domains, σ is the scattering cross section of a single domain, and d is the optical path which is in our case identical to the film thickness. Following equation (1) the logarithm of the transmission is expected to decrease linearly with film thickness if the product of N_v and σ is constant for a given LMWLC concentration. This behavior

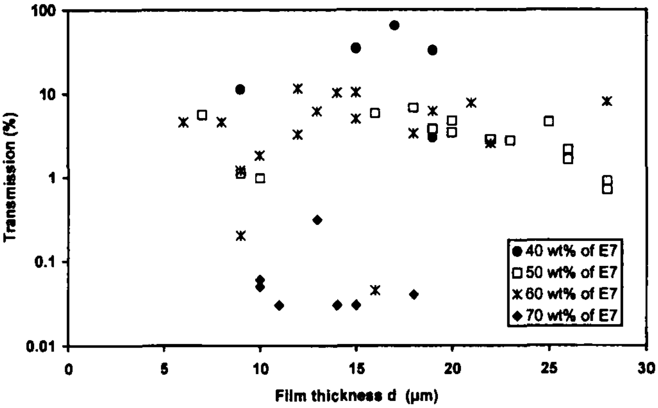

FIGURE 1 Initial optical transmission on a logarithmic scale versus film thickness of PDLC films (λ=632.8 nm). The LMWLC content was varied from 40wt% to 70wt%.

was indeed generally found for samples possessing 50 wt% and 60 wt% LMWLC. The transmission values of the 40 wt% E7 films are somewhat scattered indicating low droplet densities and probably inhomogeneously distributed droplets of small size. As a consequence light is not scattered effectively for 40 wt% LMWLC samples. On the other hand samples containing 70 wt% of E7 strongly scatter light leading to lower transmission values compared to the 50 and 60 wt% LMWLC samples. In all cases discussed here, the transmission values in the initial off-state were substantially lower than those measured in the off-states after subsequent application of voltage cycles. One should note that the second and all following applications

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of voltage scan cycles generally did not change furthermore the transmission in the off-state compared to the values obtained after the first cycle was completed. Figure 2 illustrates the evolution of the

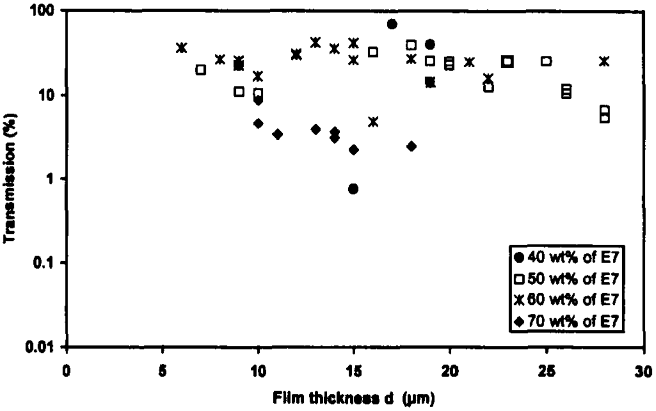

FIGURE 2 Influence of the LMWLC content on the transmission in the off-state (after application of several voltage cycles) of PDLC films as a function of film thickness (λ=632.8 nm).

final transmission in the off-state after application of several voltage cycles. The same series of samples and LMWLC concentrations as in Figure 1 has been considered. The observation that some residual transparency is preserved after the electrical field is removed is described in literature as memory effect[7]. The LMWLC molecules do not completely relax back to their original scattering state and partially tend to maintain their anchoring at the LMWLC domain/polymer interface even after the field is removed. The effective refractive index of this part of the LC domains is more close to the polymer matrix leading to enhanced transmission values.

Figures 1 and 2 also show that the experimental data can be

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roughly described by linear relationships as mentioned above but such straight lines will not easily pass through the point *d*=0/*T*=100% especially for samples containing 70wt% LMWLC. These findings indicate that the approximation of independently scattering LC domains might not be valid in the total range of sample thicknesses covered by the experiments. The results can be explained by an effect of multiple light scattering for film thicknesses exceeding roughly 10-15 μm. As an example, the effect of film thickness on threshold and saturation voltages V_{10} and V_{90} is shown in Figure 3 for the LMWLC concentration of 50wt%. V_{10} and V_{90} represent the voltages required for obtaining 10 and 90% of the maximum transmission value, respectively. Figure 3 illustrates that an increase in the film thickness results in a linear increase of V_{10} as well as of V_{90}. These results are consistent with

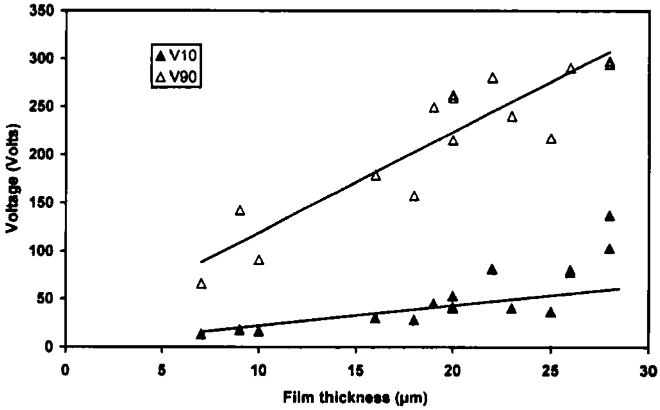

FIGURE 3 Threshold (V_{10}) and saturation (V_{90}) voltages as functions of film thickness for a LMWLC concentration of 50wt% (first voltage cycle, ramp up, λ=632.8nm, λ=145Hz).

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the theoretical proportionality between these two quantities and the film thickness whatever the droplet configuration[8].

In many cases linear polymer/LMWLC mixtures do not show reproducible electro-optical results such as those found in this study. Investigations have been performed for example on mixtures of linear poly(n-butylacrylate) (polyAbu) of molecular weight M_w=112 000 g/mol and E7[9]. By applying several voltage cycle scans on this system the electro-optical properties continue to change and considerable relaxation effects were found. The polyAbu/E7 system represents certainly a higher miscibility between polymer and LMWLC than the system under investigation and the polyAbu exhibits a glass transition at low temperature (T_g=-55°C). On the other hand PVDF-HFP/E7 mixtures are characterized by a wide miscibility gap at room temperature in the range of LMWLC contents considered here. Furthermore the semicrystallinity of the copolymer can still be observed in the presence of a concentration as high as 70wt% of E7. These findings are probably the reason for the observed reproducible electro-optical behavior.

CONCLUSIONS

The electro-optical properties of blends made of the copolymer PVDF-HFP and the LMWLC E7 were investigated. Transmission versus voltage curves are strongly related to film thickness and LMWLC concentration. Low transmission values in the initial off-state were obtained for samples containing 50 to 70wt% of LMWLC. Reproducible electro-optical properties were obtained for 50 and 60wt% LMWLC samples in spite of the presence of a linear polymer building up a physical network structure. Such results are usually only obtained from systems involving chemically crosslinked polymer matrices[10]. Further studies are in progress to investigate the relationship between sample morphology and the electro-optical properties.

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